Supporting Information

Self-aggregated perfluoroalkylated hexa-*peri*-hexabenzocoronene fibers observed in cryo-SEM and fluorescence

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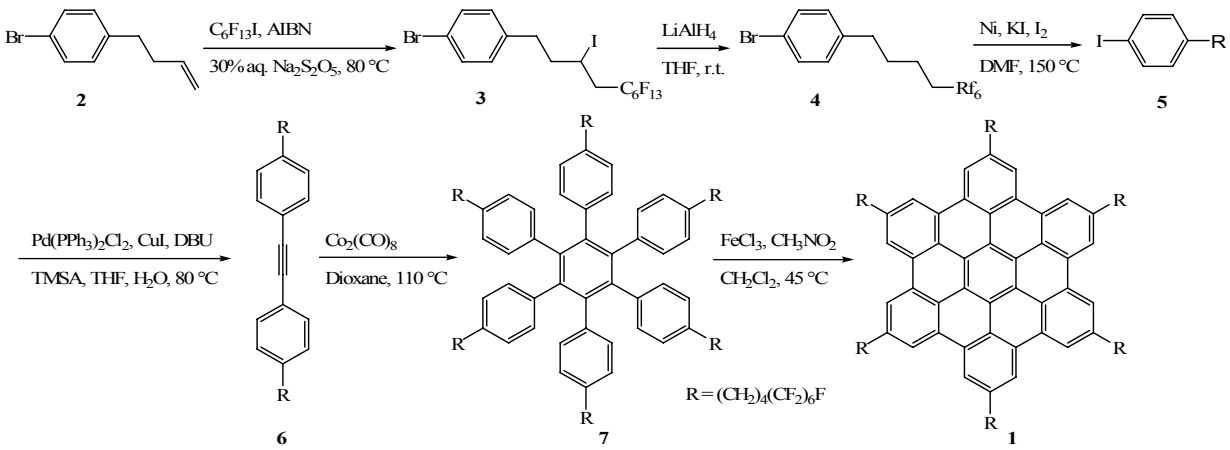
Experimental section

General Methods:

All reagents and solvents were purchased from commercial sources and used without further purification. THF and dichloromethane were additionally dried by the Grubbs method. All reactions were performed under inert atmosphere (N_2 or Ar). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 360 or a Bruker DRX 500, using $CDCl_3$ or hexafluorobenzene as solvent. Chemical shifts (δ) are reported in ppm, whereas coupling constants (*J*) are given in Hz. Mass spectra were recorded on a Finnigan Thermo Quest GC/MS Voyager spectrometer. MALDI-ICR spectra were measured on a Bruker 4.7 T BioAPEX II FT/ICR spectrometer using a 337 nm nitrogen laser and trans-2-[3-(4-*t*-butyl(phenyl)-2-methyl-2-propenyliden]-malonitril (DCTB) as matrix. As cryo-SEM system a Gatan ALTO 2500 installed on a Philips XL30 ESEM FEG microscope was used. Absorption spectra were recorded on a Cary 6000i (Varian) spectrophotometer and emission and excitation spectra were measured on a Spex-Fluorolog-3-system. Analytical TLC was performed on Merck Kieselgel 60 F254 glass pre-coated with silica gel and visualized by a $KMnO_4$ solution.

Synthesis:

The synthesis of HBC-$Rf_{4,6}$ (1) is shown in scheme 1.



Scheme S1: synthesis of HBC-$Rf_{4,6}$ (**1**)

1-Bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-3-iododecyl)benzene (3): Perfluorohexyl-iodide (2.6 g, 5.86 mmol) was syringed in a round bottomed flask equipped with a reflux condenser before the reaction system was heated to 50 °C. A 30 % aqueous solution of $Na_2S_2O_5$ (1 mL) was

then added, followed by addition of AIBN (19 mg, 0.11 mmol) and 1-bromo-4-but-3-enylbenzene (1.2 g, 5.68 mmol). The reaction mixture was heated to 80 °C for 4 hours. After the addition of water (20 ml) the product was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were washed with water (3 x 50 mL), dried over Na_2SO_4, filtered and evaporated to afford **3** (3.67 g, 98 %) as colourless oil. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.42 (*d*, *J* = 8.2 Hz, 2 H, Ar), 7.09 (*d*, *J* = 8.2 Hz, 2 H, Ar), 4.23 (*tt*, 1 H, *J* = 8.6 Hz, *J* = 5.0 Hz, CHI), 2.48-3.04 (*m*, 4 H, CH_2), 2.00-2.17 (*m*, 2 H, CH_2). ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 138.78, 131.70, 130.24, 107.56-121.07 (*m*, Rf_6), 120.21, 41.69 (*t*, *J* = 21.1 Hz), 41.39, 35.13, 19.71. MS (EI, 70 ev): m/z (% int.) = 89.9 (75), 116.9 (44), 170.8 (100), 529.6 (13), 656.9 (5) [M^+].

1-Bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)benzene (4):

To a slurry of $LiAlH_4$ (574 mg, 15.1 mmol) in THF (5 mL) was added 1-bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,10 -tridecafluoro-3-iododecyl)-benzene (**3**) (5.0 g, 7.56 mmol) in THF (10 mL). After three hours of reaction at room temperature the mixture was quenched by the addition of H_2O (5 mL), 1M NaOH (5 mL) and H_2O (15 mL). The suspension was filtrated and washed exhaustively with ether. The organic phase separated, washed with water, dried over Na_2SO_4, filtrated and evaporated. Purification was achieved by silica gel column chromatography using pentane as eluent, affording **4** (3.4 g, 77 %) as colourless oil. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.41 (*d*, 2 H, *J* = 8.2 Hz, Ar), 7.05 (*d*, 2 H, *J* = 8.2 Hz, Ar), 2.61 (*t*, 2 H, *J* = 7.0 Hz, CH_2), 2.01-2.15 (*m*, 2 H, CH_2), 1.61-1.73 (*m*, 4 H, CH_2). ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 140.55, 131.49, 130.08, 119.73, 108.10-121.99 (*m*, Rf_6), 34.94, 30.69, 30.69 (*t*, *J* = 22.5 Hz), 19.75 (*t*, *J* = 3.6 Hz). MS (EI, 70 ev): m/z (% int.) = 91 (68), 170.8 (100), 530.7 (28) [M^+].

1-Iodo-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)benzene (5): To Ni (54.8 mg, 0.94 mmol), KI (62 mg, 0.37 mmol), I_2 (2.3 mg, 9.3 μmol) and deoxygenated 1-bromo-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-decyl)benzene (**4**) (0.1 g, 0.19 mmol) was added DMF (0.5 mL). This suspension was heated to 150 °C for 27 hours. The crude reaction mixture was allowed to cool to room temperature, before 3 % HCl (10 mL) was added. The resulting mixture was extracted with pentane (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered and all volatiles were removed yielding a brown liquid, which was filtered over a plug of silica gel under reduced pressure using pentane as eluent, affording **5** (90 mg, 83 %) as colourless

liquid. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 7.61 (*d*, 2 H, *J* = 8.2 Hz, Ar), 6.93 (*d*, 2 H, *J* = 8.2 Hz, Ar), 2.60 (*t*, 2 H, J = 7.04 Hz, CH_2), 2.00-2.15 (*m*, 2 H, CH_2), 1.61-1.71 (*m*, 4 H, CH_2). ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 141.22, 137.47, 130.44, 107.65-121.48 (*m*, Rf_6), 90.98, 35.03, 30.65, 30.68 (*t*, *J* = 22.5 Hz), 19.76 (*t*, $^{3}J_{CF}$ = 3.64 Hz). MS (EI, 70 ev): m/z (% int.) = 91.0 (21), 216.9 (100), 578.8 (12) [M^+].

1-(5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodecyl)-4-{[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-trideca-fluorodecyl)phenyl]ethynyl}benzene (**6**): CuI (326 mg, 1.71 mmol) and $PdCl_2(PPh_3)_2$ (721 mg, 1.03 mmol) were suspended in an oven dried Schlenk reaction vessel in THF (40 mL). 1-iodo-4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-decyl)benzene (**5**) (9.9 g, 17.12 mmol) was dissolved in THF (40 mL) before being added into the reaction vessel followed by injection of DBU (15.35 mL, 103 mmol). H_2O (123 µL, 6.85 mmol) and TMSA (1.32 mL, 9.08 mmol) were added simultaneously with two syringes. The Schlenk was then covered with an aluminium foil and heated to 80 °C. After 72 hours of reaction the black reaction mixture was allowed to cool to room temperature before ether (50 mL) was added. The crude mixture was extracted with H_2O (2x 50 mL), 10% HCl (50 mL), brine (50 mL) and H_2O (50 mL). The combined organic fractions were dried over Na_2SO_4, filtered and evaporated yielding a brown solid which was dissolved in ether / pentane 9:1 (400 mL) and filtered over a plug of basic aluminium oxide under reduced pressure. After evaporation of all volatiles a yellow solid was obtained which was further purified by recrystallization from pentane / ether / ethanol yielding **6** (3.5 g, 44 %) as off-white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (*d*, 4 H, *J* = 8.1 Hz, Ar), 7.15 (*d*, 4 H, *J* = 8.1 Hz, Ar), 2.67 (*t*, 4 H, *J* = 7.5 Hz, CH_2), 2.05–2.14 (*m*, 4 H, CH_2), 1.68-1.76 (*m*, 8 H, CH_2). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 141.89, 131.65, 128.37, 121.00, 88.96, 105.63-121.06 (*m*, Rf_6), 35.45, 30.72 (*t*, *J* = 22.1 Hz,), 30.62, 19.79. MS (EI, 70 ev): m/z (% int.) = 565.9 (100), 928.0 (15) [M^+].

Hexakis[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]benzene (7): 1-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)-4-{[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-decyl)-phenyl] ethynyl}benzene (**6**) (2.8 g, 3.02 mmol) was dissolved with dioxane (180 mL). $Co_2(CO)_8$ (62.16 mg, 0.18 mmol) was added before the reaction mixture was heated to 110 °C. After 48 hours the reaction mixture was cooled to room temperature and all volatiles were removed yielding a brown solid. Filtration through a plug of silica gel under reduced pressure using ether as solvent removed

all traces of the catalyst and yielded a yellow solid which was recrystallized from ether / ethanol yielding **7** (2.52 g, 90 %) as white solid. ^{1}H NMR (360 MHz, $CDCl_3$): δ = 6.68 (*d*, 12 H, *J* = 7.9 Hz, Ar), 6.62 (*d*, 12 H, *J* = 7.9 Hz, Ar), 2.39 (*t*, 12 H, *J* = 7.0 Hz, CH_2), 1.89-2.04 (*m*, 12 H, CH_2), 1.46-1.53 (*m*, 12 H, CH_2), 1.34-1.45 (*m*, 12 H, CH_2). ^{13}C NMR (90.55 MHz, $CDCl_3$): δ = 140.19, 138.53, 137.85, 131.58, 126.45, 108.07-121.19 (*m*, Rf_6), 34.62, 30.55 (*t*, *J* = 22.5 Hz), 30.38, 18.96. MALDI-ICR-MS (DCTB, solvent free preparation): m/z (% int.) 2778.45 (92) [$M^{\bullet+}$, 92 %; calcd for $C_{102}H_{72}F_{78}$ 2778.44].

Hexakis(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)hexabenzo[bc,ef,hi,kl,no,qr]coronene (**1**): Hexakis[4-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)phenyl]-benzene (**7**) (1.0 g, 0.36 mmol) was dissolved in dry CH_2Cl_2 (50 mL). At the same time a solution of $FeCl_3$ (3.5 g, 21.5 mmol) was prepared in CH_3NO_2 (20 mL). The $FeCl_3$ solution was added to the reaction mixture at 45 °C drop by drop with a syringe. Argon was bubbled through the reaction mixture by a plastic capillary during all the reaction time. After 27 h of reaction the mixture was quenched by the addition of methanol (100 mL). The black precipitate was collected by suction filtration over Millipore® and was suspended subsequently in different common organic solvents (dichloromethane, methanol, ether and pentane). The formed suspensions were each time treated in an ultrasonic bath for 30 minutes followed by refluxing for 1 h. After 2 h of cooling in the refrigerator, the suspensions were filtrated over Millipore® yielding an orange compound which was reprecipitated first from benzyltrifluoride and finally three times form hexafluorobenzene, yielding **1** as bright yellow powder (697 mg, 70 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.06 (*s*, 12 H, HBC), 3.57 (*t*, 12 H, *J* = 7.8 Hz, CH_2), 2.59-2.63 (*m*, 24 H, CH_2), 2.30 (*t*, 12 H, $^{3}J_{HH}$ = 7.8 Hz, CH_2). MALDI-ICR-MS (DCTB, solvent free preparation): m/z (% int.) 2766.33 (91) [$M^{\bullet+}$, 91%; calcd for $C_{102}H_{60}F_{78}$: 2766.34], 1906.34 (20), 1644.28 (10), 1384.27 (5%). UV/Vis: 343, 359, 370.

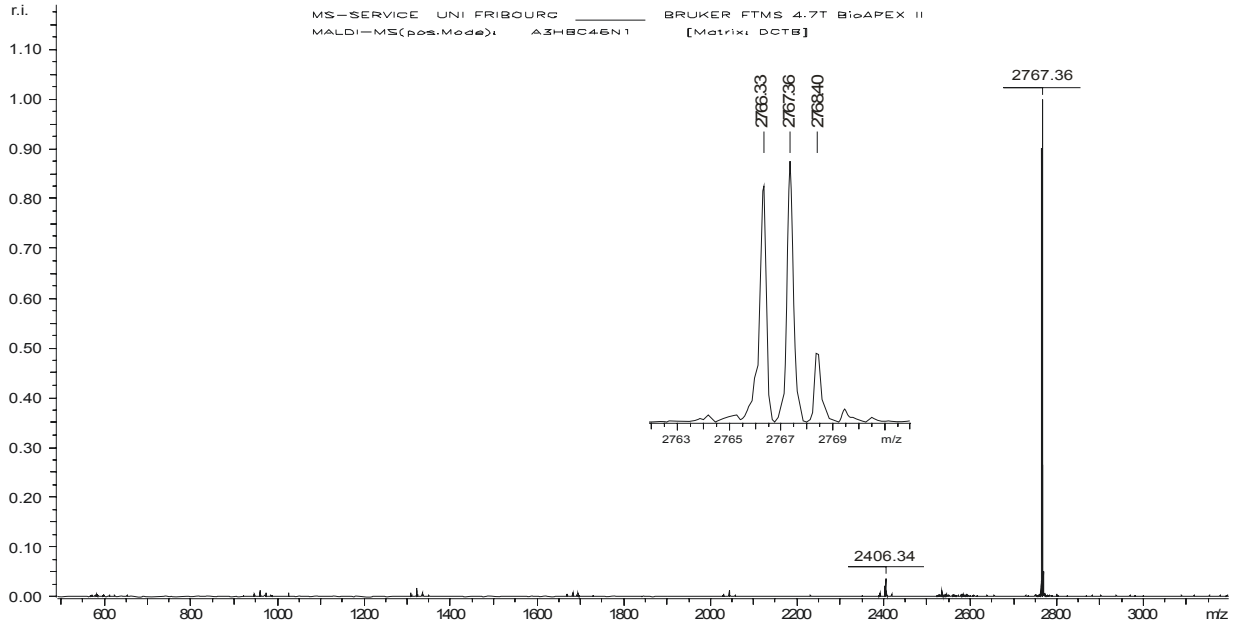


Figure S1: MALDI-ICR mass spectrum of **1**. MALDI-ICR-MS (DCTB, solvent free preparation): calculated for $C_{102}H_{60}F_{78}$ m/z (%) = 2766.34 (90), 2767.35 (100), 2768.35 (56); found: 2767.33 (90), 2766.36 (100), 2768.40 (40), 2406.34 (5).

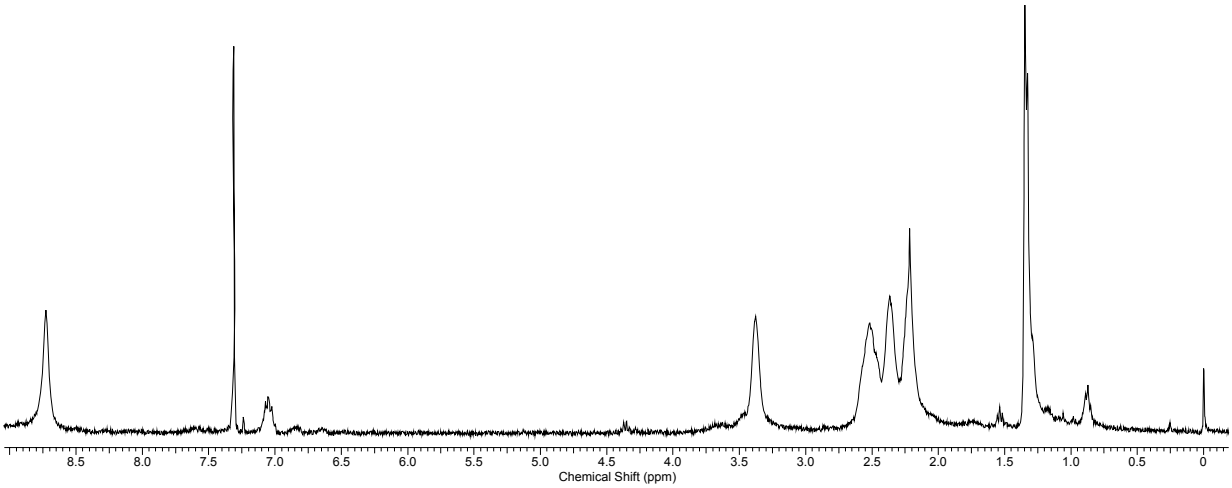
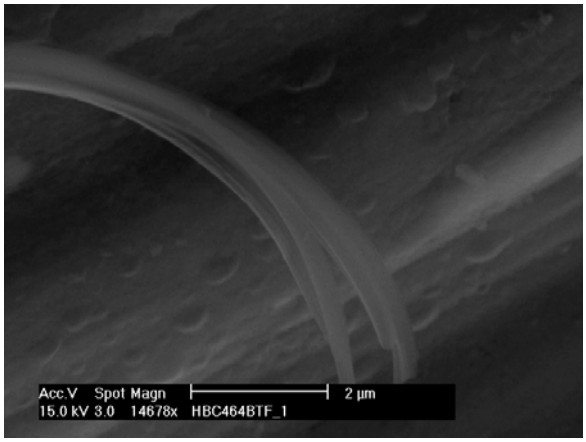


Figure S2: ^{1}H-NMR spectrum of **1** (360 MHz, hexafluorobenzol / $CDCl_3$, 25 °C)



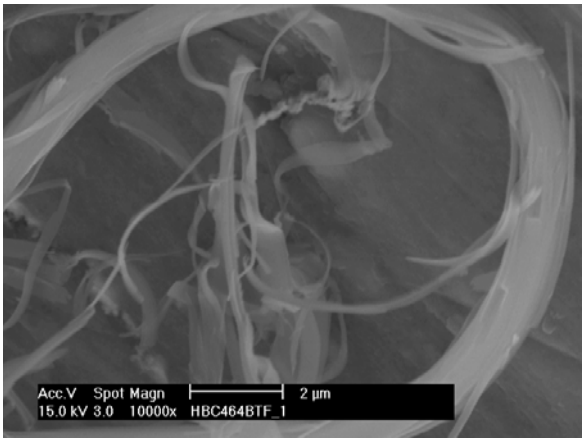
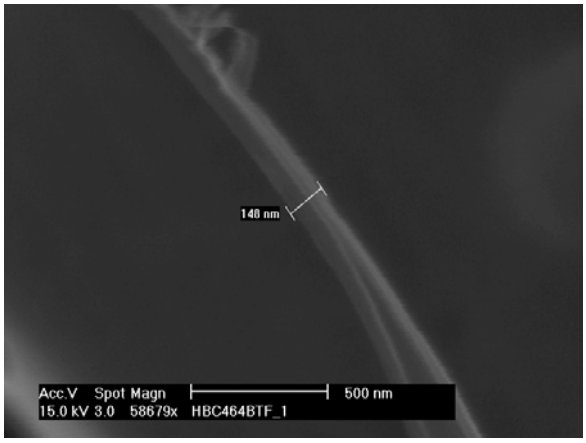


Figure S3: Micrographs obtained by cryo-SEM of HBC-$[(CH_2)_4(CF_2)_6F]_6$ (**1**) nanostructures in a BTF solution (10^{-4} M).



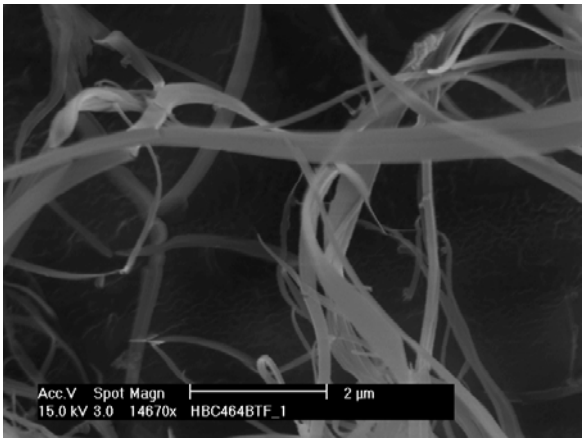
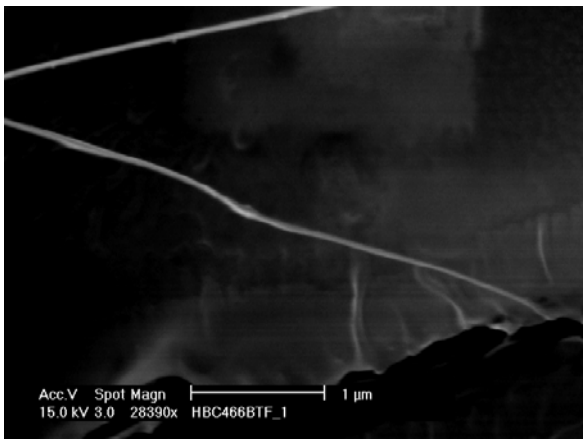


Figure S4: Micrographs obtained by cryo-SEM of HBC-$[(CH_2)_4(CF_2)_6F]_6$ (**1**) nanostructures in a BTF solution (10^{-5} M).



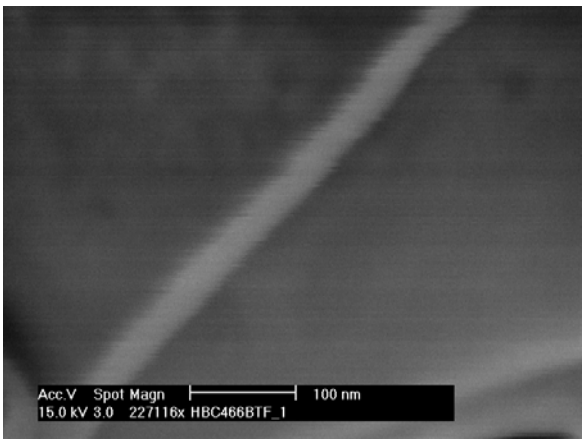


Figure S5: Micrographs obtained by cryo-SEM of HBC-$[(CH_2)_4(CF_2)_6F]_6$ (**1**) nanostructures in a BTF solution (10^{-6} M).

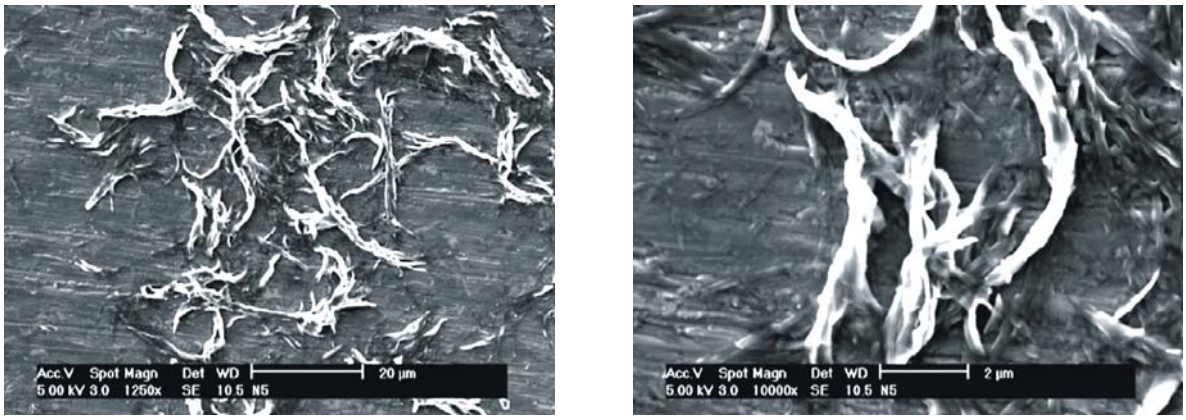


Figure S5: Micrographs obtained by SEM of HBC-$[(CH_2)_4(CF_2)_6F]_6$ (**1**) nanostructures of a BTF solution (10^{-4} M), evaporated to dryness prior to observation.

Figure S6: Micrographs obtained by cryo-SEM of HBC-$[(CH_2)_4(CF_2)_8F]_6$ nanostructures in TCB.